

LESSONS LEARNED

Treatment of Chlorinated Hydrocarbon Contaminated Groundwater
with Injectable Nanoscale Bimetallic Particles

ESTCP Project ER-0017

FEBRUARY 2009

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Environmental Security Technology
Certification Program

Report Documentation Page			Form Approved OMB No. 0704-0188	
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1. REPORT DATE FEB 2009	2. REPORT TYPE N/A	3. DATES COVERED -		
Treatment of Chlorinated Hydrocarbon Contaminated Groundwater with Injectable Nanoscale Bimetallic Particles			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
ARCADIS			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
ARCADIS			8. PERFORMING ORGANIZATION REPORT NUMBER	
Approved for public release, distribution unlimited			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
Approved for public release, distribution unlimited				
The original document contains color images.				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF: a. REPORT b. ABSTRACT c. THIS PAGE unclassified unclassified unclassified			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 8
19a. NAME OF RESPONSIBLE PERSON				

Environmental Security Technology Certification Program (ESTCP)
Treatment of Chlorinated Hydrocarbon Contaminated Groundwater with Injectable
Nanoscale Bimetallic Particles

Lessons Learned

Introduction

ARCADIS conducted a laboratory research project for the Environmental Security Technology Certification Program (ESTCP) that evaluated the reductive dechlorination of trichloroethene (TCE) by multiple types of nanoscale zero valent iron (nZVI) particles obtained from multiple manufacturers. The manufacturing methods used to produce the nZVI particles utilized during this research result in particles that fall into two structural categories that ARCADIS defined during this research including particles with amorphous atomic structures and those with crystalline atomic structures. ARCADIS has shown that structural differences in iron particles can lead to profoundly different properties during the utilization of the nZVI for reductive dechlorination of TCE. Different phases of the laboratory program focused on the, **reactivity, longevity, injectability and potential for treatment of dense, nonaqueous phase liquid (DNAPL)** for multiple manufactured types of nZVI with both amorphous and crystalline structures. Over the multiyear laboratory research program, several of the multiple vendors of nZVI contributing materials were engaged in product development/improvement efforts leading to nZVI with enhanced performance characteristics. Due to the relatively high cost of nZVI as a consumable remediation reagent, this laboratory program was aimed at investigating the factors that combine to influent return on investment including rate of reactivity, longevity under aquifer conditions, and potential to effectively treat DNAPL.

The utility of this work ultimately lies in its contributions to the field practitioner knowledge base contributing to successful application of the technology to real world problems. The core contribution is the recognition of differences between nanoscale iron particles that are supplied by different manufacturers each having unique manufacturing processes and how those differences result in different reactivity profiles for individual products. With the exception of nanoscale iron particles that are unreactive, all of the nanoscale iron products evaluated had potential utility for field use. Of particular value is the ability to differentiate products based on reactive rate, longevity, response to the aqueous geochemical environment, and type of chlorinated volatile organic compound (CVOC) contaminant [dissolved versus nonaqueous phase liquid (NAPL)] that is the target of the treatment program. This evaluation program was complex. The outline of the Lessons Learned is placed into categories to aid in clarity.

Reactivity

Reactivity is a core property of nanoscale iron particles. Rate of reaction, species participating in the reactions, and what variables are controlling those processes are critical

design parameters to provide to field practitioners. By definition reactivity is also associated with longevity since any nZVI particle is going to have a limited mass with which it can react. However, a few lessons learned that are specific to longevity are discussed in the following section.

- Design of field scale systems should carefully consider whether first order or zero order kinetics are most likely under a particular set of circumstances. Pseudo first-order kinetics was found to fit the as-received nZVI reaction results slightly better than a zero-order rate law. The majority of ZVI literature has found TCE degradation to be best described by a first-order model.
 1. The pseudo first-order TCE degradation kinetic rate constants appear to deteriorate as each nZVI ages in storage.
 2. A zero-order model results in a constant rate of TCE degradation regardless of concentration. In our studies of acid washed and/or palladized nZVI particles, zero order kinetics were observed above 2 mg/L TCE in some cases.
- Inorganic chemical species dissolved in the water of the treatment matrix also had impact on reactivity and longevity:
 1. High concentrations of carbonate cause rapid decreases in reactivity, especially for palladized irons.
 2. Exposure to waters containing high concentrations of sulfate also appears to decrease reactivity of nanoscale particles, but more slowly and less completely, than was seen either in deionized or high carbonate waters.
- Removing the surface coating of iron oxides with an acid wash will remove material from the nZVI particle resulting in smaller particles.
 1. Consistent with the literature, we have found that acid washing can improve the TCE degradation rate of milled nanoscale iron. This suggests that there is a trade off in short term reactivity of the nZVI between the higher reactivity of a freshly exposed nZVI surface over the oxide coated nZVI surface (which is also reactive) and the lower overall surface area resulting from an acid wash of the nZVI.
 2. Though acid washing was effective at improving reaction rates, it does not appear to be absolutely necessary prior to palladization of the nZVI. Acid washing can significantly reduce the amount of

palladium hydrogenation catalyst required to achieve a substantial rate increase.

Longevity

Given the price of nZVI, multiple injections are unlikely at most sites. Therefore, longevity is critical to determining end users' return on investment. This relationship between longevity and ROI makes longevity a critical parameter in the utilization of nZVI for site remediation. Longevity is governed by the reactive mass offered by a specific particle type and the rate at which that mass is consumed. It is important to take into account that many of the nZVI products available in the market are not pure iron. Iron can be deposited on silica or alumina cores, or iron particles may contain significant secondary mineral phases besides zero valent iron. The greatest longevity will be seen with nZVI products that are specifically reactive to the targeted CVOCs. In environments with high concentrations of CVOCs, longevity may not be as much of an issue as stoichiometric reaction efficiency with the CVOCs. Those lessons learned are discussed in more detail in the above section.

- Treatment efficiencies decreased dramatically over several hundred pore volumes of water flow in column tests (conducted over 18 months or less) and all of the nZVI types tested showed reduced kinetic rate constants in three years or less of storage. Thus currently available nZVI types may not be well suited for barrier applications for a dissolved plume requiring a decade or more of treatment following one injection.
- Crystalline nanoscale particles do have longer reactive lives and appear to be prone to direct reaction with CVOC rather than participation in water dissociation.

Injectability

Injectability will be of primary importance in establishing the flexibility of technologies centered around nZVI. In this context, the term 'injectability' is being used to describe nZVI injection into saturated formations. The injection of nZVI into induced fractures or fractured bedrock is not addressed. In its early phases, this project studied nZVI injectability in laboratory columns. Flowing sands created within the columns during injection simulations compromised the objectives of the laboratory scale study. It is believed that many factors will defeat attempts to obtain accurate assessments of injectability at small laboratory scale. These factors include:

- Loss of native small scale soil structure in laboratory columns that have been repacked using collected soil samples
- Typical lack of representative overpressure associated with depth in the impacted aquifer in most laboratory soil columns (though this could be remedied, it leads to a relatively more expensive laboratory study).

- Field injections are made into a three dimensional flow environment. Laboratory injection simulations are one dimensional environment. This affects simulation of the velocity of the injected nZVI solution.

For these reasons, injectability is likely studied in a more representative fashion at larger scales such as aquifer simulation “sand box” scale or at field pilot scale. Larger scale study requires significantly more fiscal commitment than is required for laboratory scale research. Measurement of injectability at either the “sand box” scale, or the field pilot scale currently involves indirect analyses as indicators of nZVI transport in the subsurface.

Typically, parameters such as contaminant reduction, pH, hydrogen, and potentially oxidation/reduction potential (ORP) have been used to indirectly infer the extent of subsurface nZVI transport during and following an injection event. The use of these parameters should be accompanied by a thorough understanding of aquifer hydrology generated through modeling and tracer testing. Tracer testing during the nZVI is also recommended though a tracer(s) should be carefully chosen to avoid inadvertent negative chemical interactions with the nZVI. Technical means to achieve direct measurement of subsurface nZVI dispersion using geophysical techniques have been theorized and proposed but not demonstrated.

At the completion of this project, it is firmly believed that the relative success of any nZVI injection is closely tied to the physical properties of nanoscale particles. Perhaps the most critical physical property expressed by many nZVI types is the tendency for multiple individual particles to agglomerate into large groupings of particles. This process is detrimental to injection efforts since larger aggregate particle sizes that are more difficult to transport through the target aquifer are generated. Tendencies for nZVI to agglomerate appear to vary with product and manufacturers/researchers are investigating multiple technical means to control agglomeration. Some agglomeration control strategies may prove detrimental to the reactivity of the nZVI product to which they are applied. Agglomeration characteristics must be considered when applying the concept of “shelf life” of nZVI products.

Dense Nonaqueous Phase Liquid Treatment

The ability to treat dense nonaqueous phase liquid (DNAPL) is an important element of the utility of nanoscale iron particles. It may prove to be its dominant mode of application in the field. Stochiometric efficiency is typically desired over absolute longevity.

- This study clearly shows that DNAPL can be treated with nZVI without the presence of an oil emulsion. Results for at least one nZVI type tested suggest that substantial (50%) treatment of DNAPL phase CVOCs was achieved in less than one month. This occurred without the injection of an oil phase which others have argued is required for effective treatment of DNAPL with nZVI.
- The presence of elevated chloride in the treatment environment appears to enhance kinetics in dissolved phase systems and stochiometric reaction

efficiency in the presence of DNAPL. In the case of DNAPL treatment the chloride effect was almost as significant as the effect of palladium.

1. The presence of chloride had a greater effect on the amorphous particles than the crystalline particles under conditions where iron oxides were formed (with deionized water) or sulfates were present.
 2. Column tests and DNAPL treatment experiments all suggest that the presence of chloride (either natural or from CVOC degradation) can provide some at least temporary protection of amorphous irons from passivation. This effect was less often observed with crystalline irons.
- The use of palladium to create a bimetallic particle appears to significantly enhance the longevity and stoichiometric reaction efficiency of nZVI types tested in the presence of DNAPL.

Class 1 Reactive Particles Driven by Water Dissociation vs. Class Two Particles Driven by Adsorption Processes

There are two fundamental types of nanoscale iron particles available, those with an amorphous structure and those with a crystalline structure. Knowledge and understanding of the consequences of those structural differences are important to field practitioners. Options are available to more efficiently manage treatment of CVOCs as a dissolved phase or as DNAPL in a variety of environments.

- There are fundamentally two types of nanoscale iron particles currently available, those with an amorphous structure and those with a crystalline structure.
 1. Those that have amorphous structure have the highest intrinsic reactivity typically demonstrated by the visible generation of hydrogen gas in the presence of water. These particles have been termed Type 1 in this evaluation. This initial high level of reactivity in general does not translate into a particle with longevity. These materials are the reductive equivalent to chemical oxidants, suitable for treatment of compounds subject to reduction such as CVOCs in source areas or zones of high adsorbed concentrations adjacent to source areas.
 2. Those nZVI types with a more crystalline structure do not have as high an intrinsic initial reactivity. Water dissociation likely plays a minor role for these materials. It is likely that reaction rates are dominated by adsorption of the CVOC directly to the iron surface and subsequent dehalogenation via electron transfer directly from metallic iron. The tendency is for the iron to be only consumed by

direct reaction with the CVOC (and other reactive dissolved species including inorganics such as sulfate and carbonate). These materials may have some potential for the treatment of dissolved phase CVOC contamination. These particles can be used in source areas as well but will show less rapid CVOC mass removal.

- There is also evidence that Class 2 reactivity can be stimulated in Class 1 particles due to surface effects. The presence of iron oxide coatings or coatings of other reaction products or possibly even an engineered system using surface active reagents can act as a means to imprint Class 2 behavior, likely by modification of surface adsorption processes. In application, these materials may have some potential for the treatment of dissolved phase CVOC contamination if passivation by side reactions with inorganic species can be minimized.

Non-Reactive Particles

- There were examples of amorphous nZVI particles tested during this laboratory program that had no observable reactivity towards CVOCs at all. Limited initial TCE removal was observed, with subsequent rebound or leveling of the TCE concentration. This indicates that there was some adsorption of TCE to these materials, but no reactions took place. Likely this is due to blinding from dispersants, surfactants or other reagents that were used for the particular manufacturing process used for those tested materials.
- The field use of additives to a mixture containing nanoscale iron can cause unexpected dramatic decreases in performance and thus must be carefully evaluated before implementation.

Summary and General Observations

These lessons are focused on first principals and dominant characterizations of the nZVI types evaluated that are important early considerations for product selection by field practitioners.

- Site specific treatability testing is required to determine if the treatment regimes required to meet the design objectives can be achieved with a given combination of nanoscale iron and aqueous geochemistry. General rules of thumb to guide application can be elucidated. Initial rates will generally be most rapid for irons with high surface area, amorphous character and recent manufacturing date.
- The initial rates of reaction of different batches of iron provided by the same manufacture under the same brand name can differ dramatically. This likely reflects that the manufacturing technology is continuing to evolve. This is one

currently important reason we recommend that each individual batch of iron undergo kinetics testing as a quality control step before application in the field.

- All of the tested nanoscale iron products generated visible evolution of a gas, believed to be hydrogen, during acid washing and several nZVI products did so before acid washing. This suggests that safety precautions are necessary during storing, shipment and application. **The increasing rigor of Department of Transportation regulations governing transport of materials of this type makes this a critical consideration for use.**
- Exposure to water causes a decline in reactivity likely due to water dissociation. This means that nZVI products manufactured and/or shipped in aqueous solutions are at a disadvantage with regards to reactive life compared to particles that are manufactured and shipped as non-aqueous dispersions. This also has impact on shipping methods and packaging that are becoming increasingly restrictive.
- Both types of particles can likely be used for the treatment of source zones, or high concentration zones adjacent to source areas. The amorphous particles are likely best used in source areas only.
 1. Conditions where potential for hydrogen transport out of the treatment zone is low or conditions where contemporaneous biological treatment via stimulation with carbon substrates is taking place are likely preferable for the amorphous materials.
 2. The crystalline particles are more suitable for high flow conditions or completely abiotic treatment.
- Contrary to original belief, in almost all cases the TCE removal performance of nZVI particles was better in the non-palladized form compared to palladized particles.

The data used to make these conclusions is included in comes from detailed reports generated during this project supplemented by the available literature.